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POLLUTION ABATEMENT: RECLAMATION OF RED PHOSPHORUS SMOKE COMPOSITION

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Chemical processes are described which offer various techniques as means to reclaim certain ingredients in waste red phosphorus pyrotechnic smoke composition or to convert the waste composition to useable and/or ecologically "clean" by-products.

Laboratory test data are provided which demonstrate that pyrolusite, one of the ingredients in the waste composition, is not manganese dioxide

as commonly thought in the pyrotechnic field.

One developed technique of reclamation provides a soil additive product (liquid form) which contains 4.4% P_4O_{10} (phosphoric anhydride), 1.8% N_2 (soluble nitrogen), 0.8% manganese; 0.25% magnesium and 0.1% zinc. Ten gallons of this solution is being field-tested by Purdue University agronomists.

SUMMARY

The purpose of this work was to explore the physical and chemical processes involved in the reclamation and/or disposal of the ingredients of Navy pyrotechnic devices. This year's work was specifically directed at devices containing red phosphorus compositions such as the Mk 25 and Mk 58 marine location markers.

The Navy has pyrotechnics which require disposal in an ecologically permissible manner.

Currently the Navy has many tons of phosphorus smoke composition from scrap and non-functional pyrotechnic ordnance items such as the Mk 25, Mk 26, Mk 58 and Mk 18. Consequently, investigations leading to safe, ecologically-permissible disposal of red phosphorus smoke compositions have been completed and have resulted in a laboratory demonstration of methods for disposing of and reclaiming the pyrotechnic ingredients used in signals containing red phosphorus compositions.

Laboratory test data are provided which demonstrate that pyrolusite, one of the ingredients in the waste composition, is not manganese dioxide as commonly thought in the pyrotechnic field.

It is recommended that work should continue in defining the chemical and physical nature of pyrolusite and that alternate oxidizers should be investigated as replacements for pyrolusite, which is a foreign-source material.

With the current fertilizer shortage that exists, it is recommended that the nitric acid dissolution process be utilized in the pilot plant phase. This process produces a solution which, when adjusted to pH=8 using concentrated ammonium hydroxide solution, provides a soil additive solution which contains approximately 4.4% P_4O_{10} (phosphoric anhydride) and 1.8% N_2 (soluble nitrogen) as well as the metallic ions of manganese (0.8%), magnesium (0.25%) and zinc (0.1%). Ten gallons of this solution is being tested by Purdue University agronomists.

PREFACE

The authors wish to acknowledge the initial laboratory work of Dr. Kenneth Musselman and his assistant Mr. Robert E. Colvin, both of Naval Ammunition Depot, Crane, Indiana.

Likewise, without the support and encouragement of Dr. A. B. Amster and Mr. George Edwards of the Naval Ordnance Systems Command, Washington, D. C., this work would not have been possible.

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INTRODUCTION

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The Navy has pyrotechnics which require disposal in an ecologically permissible manner.

Currently the Navy has many tons of phosphorus smoke composition from scrap and non-functional pyrotechnic ordnance items such as the Mk 25, Mk 26, Mk 58 and Mk 18. Consequently, investigations leading to safe, ecologically-permissible disposal of red phosphorus smoke compositions were required which would result in a laboratory demonstration of methods for disposing of and reclaiming the pyrotechnic ingredients used in signals containing red phosphorus compositions.

The effort described in this report is concerned with the investigation of techniques of treating red phosphorus smoke compositions wereby either safe, ecologically permissible disposal can be obtained or efficient, economical reclamation of the ingredients can occur. The formula for this composition follows.

	% Wt.
Red Phosphorus	53
Pyrolusite ("MnO_2")	34
Magnesium	7
Zinc Oxide	3
Linseed Oil	3
	100

APPROACHES

Nitric Acid Dissolution

Samples of red phosphorus smoke composition were treated with aqueous solutions of nitric acid (HNO_3) ranging in concentration from 10% HNO_3 up to 70% HNO_3 ("concentrated" HNO_3). Normally, the reactions with the HNO_3 solutions were carried out at temperatures near or above 100° Centigrade for at least thirty minutes.

At levels of concentration below 20% HNO_3, incomplete sample dissolution occurred. Above 20% HNO_3 concentrations, sample dissolution occurred more completely as HNO_3 concentration was increased. However, it was discovered that if concentrations of 45% HNO_3 or greater were employed, spontaneous fires occurred quite regularly as the HNO_3 solution was added to the samples. This hypergolic reaction could be accounted for by the following reactions:

(1) The hydrolysis of red phosphorus

$$2P_4 + 12\ H_2O \xrightarrow{HNO_3} 3\ H_3PO_4 + 5\ PH_3\uparrow$$

(2) The rapid oxidation of phosphine

$$2\ PH_3 + 4\ O_2 \longrightarrow P_2O_5 + 3\ H_2O$$

This latter reaction is catalyzed by HNO_3, steam in the presence of metal catalysts, and NO and NO_2 gases which would be present from the thermal decomposition of HNO_3 in the first reaction.[1]

From extensive laboratory tests (see Table 1), the optimum dissolution of the red phosphorus smoke composition (RPC) occurred when an 8-gram sample was mixed with 53 milliliters of 35% nitric acid and heated at 105°C for a duration of 75 minutes to 120 minutes. The time of heating varied in somewhat direct proportion to the size of the largest RPC aggregate in the 5-gram sample.

Care needs to be taken that the RPC is not added too rapidly to the acid solution. The very exothermic reaction between the magnesium and acid produces a rapid rise in the temperature of the acid solution and excessive foaming due to

TABLE 1

SUMMARY OF EVALUATION OF ACID DIGESTION UPON CHEMICAL INGREDIENTS UTILIZED IN RED PHOSPHORUS SMOKE COMPOSITION

Experiment Number	Reactants	%w Each Component In Mixture	Acid Utilized[c]	%w Residue[d] Theoretical	Actual	% Variance From Theory
1	P_1[a]	100.00	35% HNO_3	0	0.15	0.15
2	P_2[b]	100.00	"	0	1.48	1.48
3	P_1 Mg (Gran 6)	87.09 12.91	" "	0	0.68	0.68
4	P_2 Mg	87.11 12.89	" "	0	3.77	3.77
5	P_1 ZnO	93.06 6.94	" "	0	0.51	0.51
6	P_2 ZnO	93.06 6.94	" "	0	4.24	4.24
7	P_1 MnO_2	61.36 38.64	" "	38.64	3.43	-35.21
8	P_1 MnO_2	61.36 38.64	" "	38.64	10.27	-28.37

TABLE 1 (Cont.)

SUMMARY OF EVALUATION OF ACID DIGESTION UPON CHEMICAL INGREDIENTS UTILIZED IN RED PHOSPHORUS SMOKE COMPOSITION

Experiment Number	Reactants	%w Each Component In Mixture	Acid Utilized[c]	%w Residue[d] Theoretical	%w Residue[d] Actual	% Variance From Theory
9	P_1	58.68	35% HNO_3	36.96	4.14	-32.72
	MnO_2	36.96	"			
	ZnO	4.36	"			
10	P_2	58.67	"	36.98	8.31	-28.67
	MnO_2	36.98	"			
	ZnO	4.35	"			
11	P_1	56.17	"	35.36	3.88	-31.58
	MnO_2	35.36	"			
	Mg	8.37	"			
12	P_2	56.18	"	35.48	8.02	-27.46
	MnO_2	35.48	"			
	Mg	8.34	"			
13	P_1	54.02	"	34.08	6.12	-27.96
	MnO_2	34.08	"			
	Mg	7.94	"			
	ZnO	3.96	"			
14	P_2	54.02	"	33.97	8.01	-25.95
	MnO_2	33.97	"			
	Mg	7.94	"			
	ZnO	4.07	"			

TABLE 1 (Cont.)

SUMMARY OF EVALUATION OF ACID DIGESTION UPON CHEMICAL INGREDIENTS UTILIZED IN RED PHOSPHORUS SMOKE COMPOSITION

Experiment Number	Reactants	%w Each Component In Mixture	Acid Utilized[c]	%w Residue[d]		
				Theoretical	Actual	% Variance From Theory
15	Hooker Composition Pressed	---	"	34.0	2.76	-31.00
16	Hummel Composition Pressed	---	"	34.0	12.43	-22.00
17	MnO_2	100.00	"	100.00	87.51	-12.49
18	MnO_2 Mg	80.94 19.06	" "	80.94	60.60	-20.28
19	MnO_2 ZnO	87.42 12.58	" "	87.42	68.79	-18.63
20	MnO_2 Mg ZnO	73.91 17.39 8.70	" "	73.91	51.65	-22.26
21	MnO_2	100.00	85% H_3PO_4	100.00	100.00	0.0
22	MnO_2	100.00	20% H_3PO_4	100.00	100.00	0.0

TABLE 1 (Cont.)

SUMMARY OF EVALUATION OF ACID DIGESTION UPON CHEMICAL INGREDIENTS UTILIZED IN RED PHOSPHORUS SMOKE COMPOSITION

Experiment Number	Reactants	%w Each Component In Mixture	Acid Utilized[c]	%w Residue[d]		
				Theoretical	Actual	% Variance From Theory
23	MnO_2	100.00	85% H_3PO_4 35% HNO_3 (1:4)	100.00	98.98	-1.02
24	P_1 MnO_2	61.23 38.77	20% H_3PO_4 "	100.00	61.67	-38.33
25	P_2 MnO_2	61.48 38.52	" "	100.00	57.15	-42.85
26	P_1	100.00	85% H_3PO_4	100.00	93.75	-6.25
27	P_1 MnO_2	61.38 38.62	85% H_3PO_4 35% HNO_3 (1:4)	38.62	4.96	-33.66
28	P_2 MnO_2	61.37 38.63	" "	38.63	12.33	-26.30

a P_1 = Hooker Red Phosphorus, Technical.

b P_2 = Hummel Red Phosphorus, Aluminized (2.86%).

c Digestion conducted 30 minutes at 105°C.

d Actual values are averages of two or more determinations.

the hydrogen released will occur. Proper venting of the hydrogen gas in a pilot plant process will be necessary to eliminate the potential explosive mixture of hydrogen and air. Hydrogen-air mixtures have a very wide range of explosive limits. A potentially explosive mixture exists with as little as 5% hydrogen in air.[2]

The dissolution of the sample occurs with an open beaker where a reduction in solution volume can occur or under reflux conditions where no moisture loss can occur. If the "open beaker" technique is used, it is important that the solution volume is not reduced by more than 40% since insoluble materials begin to come out of the solution.

The dissolution is complete when the red color of the phosphorus is no longer visible in the solution.

The chemistry involved is straightforward with the one exception being the pyrolusite.[3]

(1) $Mg + 2H^+ \longrightarrow Mg^{++} + H_2\uparrow$

(2) $ZnO + 2H^+ \longrightarrow Zn^{++} + H_2O$

(3) $P_4 + 6\ H_2O \longrightarrow 2\ HPO(OH)_2 + 2PH_3\uparrow$

$HPO(OH)_2 + H_2O \longrightarrow OP(OH)_3 + H_2\uparrow$

$PH_3 + 4H_2O \longrightarrow OP(OH)_3 + 4H_2\uparrow$

The pyrolusite, which normally is considered to be manganese dioxide (MnO_2), reacts in the following manner.

Half-cell reactions:

(4) $MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{++} + 2H_2O$

(5) $P_4 + 12\ H_2O \longrightarrow 12e^- + 20\ H^+ + 4HPO_3^=$

Overall:

(6) $6MnO_2 + 4H^+ + P_4 \longrightarrow 6Mn^{++} + 4HPO_3^=$

Normally, one would not expect the pyrolusite to be dissolved in nitric acid[4] but, in the presence of the red phosphorus, the redox reaction (6) occurs.

The particular properties of pyrolusite will be discussed in a later section of this report.

Hydrochloric Acid Dissolution

Using concentrated hydrochloric acid solution (36% HCl), vigorous reactions with samples of red phosphorus smoke composition were observed. No spontaneous fires occurred. In all cases, residues of primarily red phosphorus remained.

When pyrolusite was treated with concentrated HCl solution for thirty minutes at 105° Centigrade, 0.8%-0.9% residues resulted as compared to the original sample weight of pyrolusite. The evolution of chlorine was observed. This would indicate that the residue remaining when a red phosphorus smoke composition sample was treated with concentrated HCl should be 99+% red phosphorus.

Experiments indicate that if a 10% HCl solution is heated at about 90° Centigrade for two hours with the red phosphorus smoke composition, dissolution of the magnesium, zinc oxide and pyrolusite is essentially complete and the residue remaining is 99+% red phosphorus.

Two-Step Acid Process

In an attempt to separate some of the ingredients from each other for reclamation purposes, samples of red phosphorus smoke composition were treated with 6% acetic acid solution and heated at 90°C for two hours. Approximately 13% of the sample dissolves when so treated. If the remaining residue is treated with a 10% HCl solution, another 37% of the sample dissolves, leaving essentially red phosphorus as the residue. If pyrolusite were MnO_2, then this process would allow the magnesium and zinc oxide to be dissolved in the first step by the acetic acid and the pyrolusite in the second step by the hydrochloric acid.

In theory, one would expect approximately 10% of the sample to dissolve in acetic acid with the two following reactions representing what should happen.

(1) $Mg + 2H^+ \longrightarrow Mg^{++} + H_2 \uparrow$

(2) $ZnO + 2H^+ \longrightarrow H_2O + Zn^{++}$

In reality, 9.0% of pyrolusite is dissolved in 6% acetic solution, this being an indication that the pyrolusite is not MnO_2. If this information is taken into account, it would be predicted that, in theory, 13.06% of a sample of red phosphorus smoke composition should be dissolved by acetic acid. Actual experimental results indicated that 12.75% of a particular sample was dissolved in 6% acetic acid.

If the separation of manganese from this composition was desired, this two-step acid process should allow about 90% recovery of the manganese present in pyrolusite. Red phosphorus as an end-product residue would also result.

One-Step Two-Acid Process

By using a 3:2 mixture of concentrated orthophosphoric acid (85% H_3PO_4) and concentrated hydrochloric acid (36% HCl) as the dissolving solvent for the red phosphorus smoke composition, a final residue of 99+% red phosphorus residue was obtained whose weight was 49.7% that of the original sample. The remaining solution, containing the metallic ions of Mg^{++}, Zn^{++} and Mn^{++} was adjusted to a pH of 8 with concentrated ammonium hydroxide and precipitates of the general form MNH_4PO_4 were obtained (where M = Mg, Zn, Mn). The yield of the MNH_4PO_4 was equal to 99.4% of the original sample weight of red phosphorus smoke composition. The solution containing the precipitate had a 500% yield of soluble phosphates. Consultation with a professional agronomist indicates that this precipitate would be an ecologically sound soil additive for agricultural uses.

Wet Oxidation Process

A process involving the controlled oxidation of a wet red phosphorus smoke composition under 800-900 psia and 450°F was investigated by NOS Indian Head.

The process yields a filtrate which is strongly acidic ($pH \geqq 1$) and some insolubles, presumably pyrolusite or a by-product thereof.

This solution could be treated with ammonium hydroxide and used as a soil additive solution.

Separation of Ingredients By Differential Densities

At the first thought, it would appear that centrifugal or flotation techniques would allow the separation of the basic ingredients of the red phosphorus smoke composition. The specific gravities of zinc oxide, pyrolusite, red phosphorus and magnesium are approximately 5.5, 5.0, 2.2 and 1.7 respectively.

However, if the specific particle size ranges of the ingredients are considered in conjunction with the densities, the terminal velocities of the particles of the ingredients are seen to overlap with each other thus making "clean" physical separation via this technique very difficult.

The terminal velocity of a rigid sphere is directly proportional to the function below:

$$V \propto \frac{D^{0.5}(d-d_s)}{dd_s}$$

where D is the diameter of the particle, d_s is density of the media and d is the diameter of the solid.

Using the densities of the ingredients, the value of

$$\frac{d - d_s}{dd_s}$$

for each ingredient is listed below, in water.

	$\left(\frac{d - d_s}{dd_s}\right)$
Zinc oxide	0.82
Pyrolusite	0.80
Red phosphorus	0.55
Magnesium	0.41

When a sample of RPC was distributed in water, a physical separation of the chiefly red phosphorus was possible by simple decanting. There was some pyrolusite and zinc oxide present in the separated material when viewed with a microscope.

This separation technique was abandoned due to the wide overlap of particle size ranges of the ingredients.

PYROLUSITE

From this investigation and previous work with RPC,[5] it has been observed that pyrolusite has chemical and physical properties which differ significantly from those same properties of a relatively pure grade of manganese dioxide.

For example, using Baker's reagent grade manganese dioxide (99.7% purity) and MIL-M-3281 pyrolusite in comparison tests, the following differences occurred.

When the two materials were separately digested for one hour at 105° Centigrade in 35% HNO_3 solution, there were residues of 87.5% of the pyrolusite and 99.8% of the manganese dioxide (MnO_2).

When similarly treated with 6% acetic acid, there were residues of 91.0% of the pyrolusite and 99.9% of the MnO_2.

When heated at 105°C for one hour in concentrated phosphoric acid (85% H_3PO_4), the MnO_2 gave no color to the acid and the pyrolusite formed a deep violet-colored solution which upon cooling yielded a gray precipitate.

The color of the pyrolusite is a deep purple-brown and the MnO_2 is a steel gray.

The magnetic susceptibility was $137X10^{-6}$ cgs units for the pyrolusite and $32X10^{-6}$ cgs units for the MnO_2, with this difference probably being due to the natural presence of iron oxides.[6]

The importance of understanding the chemical and physical nature of pyrolusite seems obvious. Not only is it helpful for the present task of reclamation/pollution abatement but, with such an understanding, it may well help explain some of the continuing problems related to the manufacture, performance and shelf-life of red phosphorus smoke compositions. Tropical storage conditions promote failures in performance[7,8] and spontaneous ignitions during storage have been observed.[9]

It is surprising that so little is known about pyrolusite when one realizes that this ingredient comprises over one-third of virtually all the Navy's red phosphorus smoke compositions.

CONCLUSIONS AND RECOMMENDATIONS

Processes have been investigated and presented which offer various possibilities as means to reclaim certain ingredients in waste red phosphorus smoke composition or to convert the waste composition to useable and/or ecologically "clean" by-products.

It is recommended that high shear stirrers be utilized in any pilot plant process. During this laboratory work, the investigators used magnetic stirrers and teflon-coated steel bars to agitate the various solutions. In order to obtain repeatable results, it was necessary to crush some composition aggregates with glass stirring rods. With high shear stirrers, composition aggregates would readily be dispersed.

It is also recommended that work should continue in defining the chemical and physical nature of pyrolusite and that alternate oxidizers should be investigated as replacements for pyrolusite, which is a foreign-source material.

With the current fertilizer shortage that exists, it is recommended that the nitric acid dissolution process be utilized in the pilot plant phase. This process produces a solution which, when adjusted to pH = 8 using concentrated ammonium hydroxide solution, provides a soil additive solution which contains approximately 4.4% P_4O_{10} (phosphoric anhydride) and 1.8% N_2 (soluble nitrogen) as well as the metallic ions of manganese (0.8%), magnesium (0.25%) and zinc (0.1%). Ten gallons of this solution is being tested by Purdue University agronomists.

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